

Chapter 15

Prescribed Fire Alters Dissolved Organic Matter and Disinfection By-Product Precursors in Forested Watersheds - Part I. A Controlled Laboratory Study

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Detritus material in forested watersheds is the major terrestrial source of dissolved organic matter (DOM) and disinfection by-product (DBP) precursors in source waters. Forest fire reduces the thickness of detritus layer and changes foliar litters into pyrogenic organic matter (PyOM) on the forest floor, resulting in different quantity and quality of DOM exported from forested watersheds. Many studies have examined DBP precursors exported from forested watersheds; however, DOM leaching from PyOM, or dissolved black carbon (BC), could have different reactivity in DBP formation compared to the DOM leaching from unburned detritus layer. Using controlled laboratory burning in this study, characteristics of foliar litters before and after burn were compared. Quality and quantity of water extractable organic matter (WEOM) from raw and burned foliar litters commonly found in the southeastern United States, including baldcypress (*Taxodium distichum*), boxelder (*Acer negundo*), longleaf pine (*Pinus palustris*), pop ash (*Fraxinus caroliniana*), sweetgum (*Liquidambar styraciflua*), and water tupelo (*Nyssa aquatica*) was compared, and evaluated for their disinfection by-product yield and specific DBP formation using a uniform formation condition test. Laboratory analysis

using pyrolysis gas chromatography mass spectrometry showed that foliar litters after burn contain significantly less lignins, nitrogenous compounds, and polysaccharides because of loss of organic matter. However, both the formula numbers and relative abundance of PAHs increased, which can be a potential health concern. Water extractable organic carbon (WEOC) and total nitrogen (WETN) decreased after burn and in particular raw material had less humic acid and fulvic acid-like compounds. PyOM aromaticity may be either enhanced or lowered by prescribed fire and highly depending upon the plant species. The specific formation of chloroform (a prevalent DBP species) decreased by 12%-60% for all plant species after burn. However, dissolved BC was more reactive in the formation of nitrogenous disinfection by-products (N-DBPs), and the specific haloacetonitriles formation increased after burn for all species.

Introduction

Forests are critically important to the supply of clean drinking water in the United States. National forests and grasslands, which represent 30% of the forest area in the U.S., provide drinking water for over 60 million people (1). The number of people served by all forests and grasslands in the U.S. are far greater than this number. Hot temperatures and longer dry periods due to climate change will increase the likelihood of larger and more severe wildfires (2). Forest fire rapidly modifies the chemical composition of the detritus layer on the forest floor, converting lignin and polysaccharide rich and relatively degradable carbon pools to polycyclic aromatic and charcoal rich and recalcitrant black carbon (BC) (3). Dissolved organic matter (DOM) leaching from pyrogenic organic matter (PyOM), or dissolved BC, could have different treatability and reactivity in disinfection by-product (DBP) formation compared to the DOM leaching from unburned detritus layer. In contrast to wildfire, prescribed fire is low-intensity burning of accumulated detritus materials to reduce the fuel amount on forest floor to prevent catastrophic wildfires (4). It is often conducted when soil is moderately moist to reduce the intensity, and it brings benefits to decrease the invasive species and release different nutrients from plant materials (5). While forested ecosystems have been identified as persistent sinks for atmospheric carbon (6), prescribed burns can affect forest's capacity to sequester carbon and carbon quality and quantity in soil organic matter pools (7, 8). For example, forest fire converts plant biomass into forms of BC such as polycyclic aromatic hydrocarbons (PAHs) that are resistant to microbial attack and persist in the soil for thousands of years (9). These new compounds are the products of incomplete combustion of biomass, which usually had lower H/C and O/C ratios (10). Hockaday, et al. (2007) (11) found that export of BC from soils via dissolution and biological transformation could constitute an important C loss mechanism. In fact, charred plant materials

can cause accelerated breakdown of simple carbohydrates (12) and enhance the loss of forest humus (13). As detritus in forest floor is one major source of terrestrial DOM (14), export of these newly formed and modified compounds is of great concern because they may alter the water quality by changing DOM quantity and quality.

The well-documented toxicological properties of DBPs suggested that exposure to DBPs in disinfected water may increase the risk of cancers such as bladder and colorectal cancers (15, 16). As DOM is an important precursor reacting with disinfectants during water treatment to yield carbonaceous (e.g., trihalomethanes; THMs) and nitrogenous disinfection by-products (N-DBPs) (e.g., haloacetonitriles; HANs) (17–19) increasing studies are focusing on the sources of DOM and the associated chlorine reactivity (20, 21). Litters have been identified as a significant watershed source of DOM contributing to the downstream water supply and DBP precursors (14, 22–24). Different plant species can have a diverse amount and composition of organic compounds such as polysaccharides, lignin, tannin, and aliphatic biopolymers (25). Thus, variation in plant species can affect the DOM composition and may affect the budget and speciation of DBPs in water treatment process. Burning of diverse plant materials would affect the quality and quantity of DOM and the subsequent DBP formation as well, which, however, has not been well studied.

In order to understand the effects of low intensity prescribed forest fire on the productions of DOM and DBP precursors in forested watersheds, we conducted a controlled laboratory study (Part I) and a controlled field study (Part II) independently. In this chapter we present Part I, the laboratory study where we compared characteristics of water extractable organic matter (WEOM) from raw and laboratory-controlled burned foliar litters of six plant species commonly found in the southeastern United States, including baldcypress (*Taxodium distichum*), boxelder (*Acer negundo*), longleaf pine (*Pinus palustris*), pop ash (*Fraxinus caroliniana*), sweetgum (*Liquidambar styraciflua*), and water tupelo (*Nyssa aquatica*), and evaluated their DBP formation using a uniform formation condition test. Results of this study would illustrate the productions of DOM and DBP precursors among different tree species under prescribed fire practices. Results of this controlled experiment would also be used to compare to the real prescribed fire practices (Part II), as described in the other chapter of Part II.

Material and Methods

Litter Collection and Black Carbon Preparation

Fresh litter samples in Congaree National Park (SC, U.S.A.) were collected using five 0.5 m × 0.5 m litterfall traps with 1 mm mesh fiberglass screen bottoms during the winter of 2010. The Congaree River drains a large portion of upstate South Carolina, and thus, can flood rapidly during heavy rain events (26). The Congaree National Park has 10 flooding events per year on average, with mean annual precipitation of 1220 mm (27). The foliar litter of six common tree species in Congaree National Park, including baldcypress (*Taxodium distichum*),

sweetgum (*Liquidambar styraciflua*), water tupelo (*Nyssa aquatica*), pop ash (*Fraxinus caroliniana*), longleaf pine (*Pinus palustris*), and boxelder (*Acer negundo*) were separated from the mixed litterfall. After collection, all litter samples were oven-dried at 50 °C for 48 hr. To simulate the burning, 10.00 g of dried litter material was placed in a pre-heated furnace at 340 °C for 4 minutes and then cooled down gradually in the muffle furnace for three hours. Samples that had flame were not put out manually during the whole process. The temperature of 340 °C has been reported to be average soil temperature in Ichauway Reserve during a prescribed fire on 1994 (28). After cooling, samples were weighed again to determine the weight lost. The burning for each plant species was conducted in triplicate. To reduce the heterogeneity of the sample, all unburned and burned litter materials were grounded and all passed through a 2-mm copper screen (20).

Chemical Characteristics of Original and Burned Litters

Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) was used to analyze the most common three litters (longleaf pine, pop ash, and sweetgum) before and after burn following the same method described in Song et al. (2010) (29). Py-GC/MS results are presented as the relative abundance of specific compound by dividing the peak area of the identified compound with the total area of all compounds. The major identified compounds were categorized into seven groups: aromatics, lignin, lipid, PAHs, phenolics, polysaccharide, and nitrogen. The detail compounds under each group were listed in Table A1.

Characterization of DOM from Litter

Water extractable organic matter (WEOM) was obtained by mixing one gram of unburned or burned litter with 200 mL Milli-Q water shaking at room temperature for 2 hr at 210 rpm. Each water extract was filtered through pre-washed 0.45 μm polyethersulfone membrane Supor-450 (Pall Corporation), and the filtrate was refrigerated at 4 °C through completion of analysis. Dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) were measured by Shimadzu TOC-V CHS analyzer. The extractability of litter material was defined as the mass of extractable organic carbon per gram original (unburned) or burned litter. The post-burn water extractable organic carbon (WEOC) yield from original litter ($\text{mg-C/g-original-litter}$) was calculated as the extractability of burned litter multiplied by the mass remaining of burned material compared to original material.

The UV-VIS absorption (UVA) spectroscopy between 200 and 700 nm was conducted using Shimadzu UV-1800 in room temperature (25 ± 1 °C) in 1 cm quartz cell. Specific ultraviolet absorbance at 254 nm (SUVA) was determined by normalizing UVA with DOC concentration and was reported in units of liter per milligram carbon per meter ($\text{L mg}^{-1} \text{ m}^{-1}$) (30). The E2:E3 ratio has been calculated as the absorbance at 250 nm divided by the absorbance at 365 nm (31). SUVA and E2:E3 ratios are considered as surrogates for aromatic carbon and molecular weight of DOM, respectively.

Fluorescence emission and excitation matrices (EEMs) were obtained using a Shimadzu RF5301 with 5 nm slit in excitation and 5 nm slit in emission. EEMs were corrected and analyzed by a numerical method, the fluorescence regional integration based on Simpson's Rule (FRI-SR) as described in Zhou et al. (2013) (32). The fluorescence regional integration (FRI) is a quantitative technique that integrates the volume beneath an EEM. Five regions in EEMs were operationally defined using consistent excitation (ex) and emission (em) wavelength boundaries based on fluorescence of model compounds, and DOM fractions: I: Aromatic Protein I (ex: 220 nm-250 nm, em: 280 nm-330 nm), II: Aromatic Protein II (ex: 220 nm-250 nm, em: 330 nm-380 nm), III: Fulvic acid-like (ex: 220 nm-250 nm, em: 380 nm-550 nm), IV: Soluble microbial by-product-like (250 nm < ex < 400 nm, em: 280 nm-380 nm), and V: Humic acid-like (250 nm < ex < 400 nm, em: 380 nm-550 nm). Volume integrated under the EEM within region I is normalized to the projected excitation-emission area and resulted in a normalized percent fluorescence response ($P_{I,n}$) (32, 33).

Disinfection By-Products Formation

The uniform formation condition (34) was the chlorination procedure used in this study and three replicates were analyzed for each litter extract. Briefly, the uniform formation condition is the condition that yields 1 ± 0.4 mg L⁻¹ free chlorine residual at pH 8 ± 0.2 after 24 hr of incubation in the dark at 20 °C after chlorination with freshly prepared NaOCl/H₃BO₃ dosing solution. Chlorine demand was calculated as the difference between chlorine dose and residual chlorine concentration after 24 h. Chlorinated samples were analyzed using headspace GC-ECD (35). Four trihalomethanes (chloroform, dichlorobromomethane, dibromochloromethane, and bromoform) and four haloacetonitriles (trichloroacetonitrile, dichloroacetonitrile, bromochloroacetonitrile, and dibromoacetonitrile) were quantified with the minimum reporting levels at approximately 0.5 µg/L. Specific DBP formation, defined as DBP concentration normalized to the initial DOC concentration, was used to evaluate the reactivity of DOC in forming DBPs and was expressed in molar units, as mmol/mol-C (20).

Statistical Analyses

All statistical analyses conducted in "R" version 2.15.0 (Copyright (C) 2012 The R Foundation for Statistical Computing). Relationships were considered to be significant at $P < 0.05$. Pearson's correlation was used to examine correlation between different parameters.

Results and Discussion

Chemical Characteristics of Litter Materials

In the spectra from Py-GCMS, both intensity and number of peaks decreased in burned litter compared to original litter, which is mainly due to the loss

of most organic matter during burning. The lignins, nitrogenous compounds, and polysaccharides all decreased for all three plant species, which can be explained by the degradation and volatilization at high temperatures (8). It has been reported that distillation of volatiles and loss of organic carbon start at temperatures between 100 and 200 °C (36, 37). Between 130 and 190 °C lignin and hemicelluloses begin to degrade, and at temperatures above 250 °C, polyaromatic structure start to form, whereas above 300 °C PAHs can be detected as well in plant char derived from cellulose, pectin, lignin and chlorogenic acid (38–40). This data matches our results considering significant decrease in lignin and polysaccharide as depicted in Figure 1. Some new peaks were observed in burned litters as well. The results indicate increases in both the abundance of PAH types (7 types of PAHs before burn to 15 types after burn) and relative abundance of PAHs (2.2% before burn and 7.7% after burn). This result is in agreement with the well-documented PAH formation in burning process (41). The percentage of aromatic compounds also increased from 15.2% to 32.3%, suggesting the formation of new aromatic structure in the organic matter. Production of these carcinogenic PAHs (42) from forest fires and prescribed burns is of great health concern to firefighters, forest workers and nearby rural communities including several Native American tribes (43, 44). The characteristics and mutagenic activities of biomass-derived PAHs from forest fires have been described, principally on the particulate matter emission to the atmosphere (45, 46).

Effect of Prescribed Fire on Carbon and Nitrogen Quantity

Comparing litters of different plant species before burning, sweetgum litter was the largest producer of water extractable organic carbon (WEOC), generating 84.62 mg-DOC per gram of litter (mg-DOC/g-original-litter), followed by longleaf pine, tupelo, baldcypress and pop ash (53.49 to 31.66 mg-DOC/g-original-litter) (Table 1). After burning, the DOC leached from burned litter decreased by 83% on average and ranged from 20.72 (longleaf pine) to 1.78 mg-DOC/g-original-litter (pop ash) (Table 1). Higher WEOC leaching from original litters was expected because they contained a greater portion of readily soluble and degradable organic C, and the burning processes caused a substantial loss of organic matter (47, 48). Thermal treatments such as prescribed fire remove preferentially external oxygen groups yielding materials with comparatively reduced solubility and colloidal properties (49, 50).

Water extractable total nitrogen (WETN) was also higher before burn, ranging from 0.36 (longleaf pine) to 1.65 mg-N/g-original-litter (boxelder) (average = 0.69 mg-N/g-original-litter), while after burn WETN ranged 0.05 (ash) to 0.87 mg-N/g-original-litter (boxelder) (average = 0.25 mg-N/g-original-litter). WETN after burn decreased mainly due to volatilizing of nitrogen. At 200 °C nitrogen starts to volatilize and above 500 °C half of the nitrogen in organic matter is lost to the atmosphere (8). The carbon to nitrogen ratio (C/N) was also calculated before and after burn. As expected, the C/N decreases after burn for all the species except for longleaf pine although both C and N quantity was decreased for this species. A positive relation between litter's weight lost after burn and initial litter C/N was observed ($r^2 = 0.69$, $p = 0.04$).

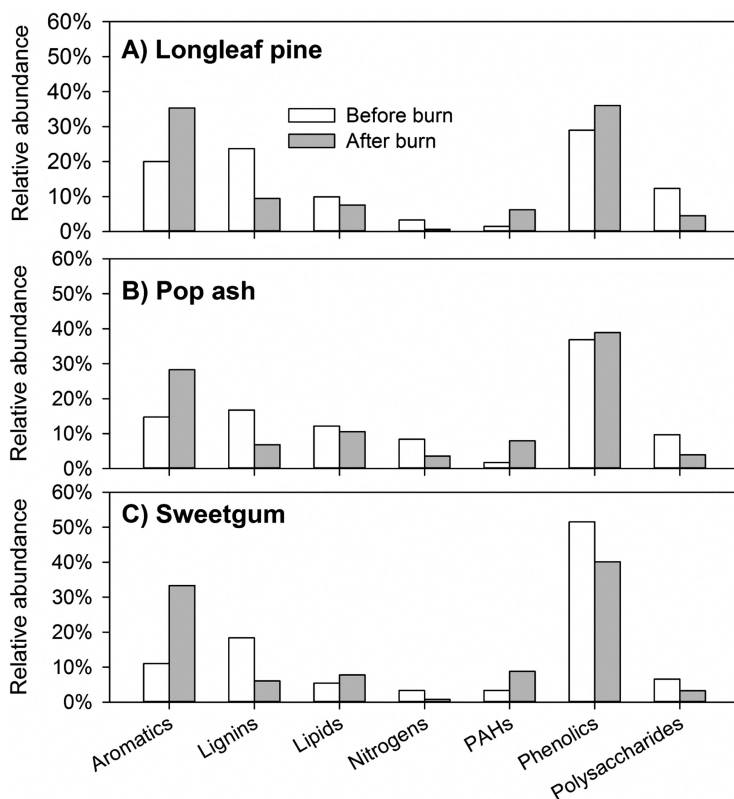


Figure 1. Chemical composition of original (white bars) and burned (gray bars) litters as determined from pyrolysis gas chromatography mass spectrometry (Py-GC/MS).

Effect of Fire on Carbon Quality

UV-VIS Spectrometry

SUVA, an indicator of the degree of aromaticity, increased significantly after burn for baldcypress, boxelder, longleaf pine, pop ash, and sweetgum except for water tupelo (Table 2). E2/E3 decrease for baldcypress, longleaf pine, pop ash, and sweet gum, but not for water tupelo and boxelder. Vergnoux et al. (2011) (44) reported that after burn WEOM exhibited both a higher aromaticity due to the increase of the hydrophilic aromaticity and lower humification and less high weighted compounds by the contribution of transphilic and hydrophobic compounds. However, our results revealed that the WEOM aromaticity of litter materials may be either enhanced or lowered by prescribed fire highly depending on the plant species. There were strong correlations between DOC and UVA both before and after burn. However, different SUVA suggested that their slopes were different before and after burn (Table 2), indicating a chemical change in

DOM occurred. While there is no correlation between DOC and SUVA ($r^2 = 0.06$, $p = 0.6$) before burn, a strong correlation can be seen after burn ($r^2 = 0.79$, $p = 0.01$) (Table 3 & Table 4). DOC from different litters appears to have more complex composition before burn in comparison to after burn, which reveals the homogenization of biomass substrate in black carbon, which is in accordance with a previous study (44) A stronger correlation between DOC and UVA after burn might be the result of homogenization as well (Table 3 & Table 4).

Table 1. Weight of Litters and Chemical Characteristics of Water Extracts of Litters before and after Burns (Means of Triplicates Are Present). One Gram of Raw Litter or Burned Litter Was Mixed with 200 mL Milli-Q Water and Shaken at Room Temperature for 2 Hours at 210 rpm.

<i>Sample</i>	<i>Weight loss</i>	<i>Pre-burn WEOC^a</i>	<i>Post-burn WEOC</i>	<i>Pre-burn WETN^a</i>	<i>Post-burn WETN</i>	<i>Pre-burn C/N</i>	<i>Post-burn C/N</i>
Bald-cypress	70.3%	35.8	6.7	0.72	0.35	57.7	21.6
Boxelder	68.6%	47.1	16.0	1.65	0.87	33.4	21.6
Longleaf pine	48.1%	62.2	20.7	0.36	0.07	200.3	348.8
Pop ash	65.8%	31.7	1.8	0.61	0.05	60.6	39.1
Sweet-gum	54.7%	84.6	3.8	0.48	0.04	206.1	103.4
Water tupelo	64.3%	53.5	3.4	0.34	0.11	183.7	34.6

^a WEOC and WETN are both in mg /g-original-litter.

Fluorescence Spectrometry

A substantial loss of organic matter was observed in region I of the EEM (Aromatic protein I). The percent fluorescence response in region I ($P_{I,n}$) ranged from 29% to 43% before burn, and decreased by 45%-87% after burn for all species (Table 2 & Figure 2). No significant changes in region II response was observed after burn except for longleaf pine. Region III and V percentages, which are related to fulvic acid-like and humic acid-like DOM, both have increased dramatically after burn (Table 2 & Figure 2). Sum of regions III and V showed an increase of 31%-76% after burn.

The more recalcitrant and aromatic structures formed by fires are derived from the alteration of carbohydrates, lipids, alkylated macromolecules, and peptides (51, 52). Consequently, some of these newly formed structures, initially non-humified, can become extractable like the humic- and fulvic- like fractions (46, 53). The FRI data reveals the difference in DOM composition before and after burning which is in accordance with our SUVA and E2:E3 data. While before burn region I exhibited high fluorescence response after burn region III and V had the highest responses except for longleaf pine.

Table 2. Optical Properties of Water Extracts of Litters before and after Burns. Fluorescence Regional Integration (FRI) Percentage Distribution of the Water Samples, SUVA, and E2/E3 Ratio.

<i>Species</i>	<i>UV-Vis properties</i>		<i>Percent fluorescence response (%)</i>				
	<i>SUVA (L/mg/m)</i>	<i>E2/E3</i>	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>
Before burn							
Baldcypress	1.32	6.19	30.52	29.49	12.53	18.39	9.07
Boxelder	1.14	4.05	29.31	31.13	15.75	15.66	8.16
Longleaf pine	1.01	9.24	43.08	29.21	7.11	16.65	3.94
Pop ash	1.55	4.92	39.16	28.29	11.86	15.20	5.49
Sweetgum	1.93	5.28	38.19	33.10	9.11	15.36	4.24
Water tupelo	2.56	4.89	37.05	29.95	13.55	12.37	7.09
After burn							
Baldcypress	2.09	5.42	12.00	30.84	29.11	14.56	13.49
Boxelder	2.07	5.56	10.83	32.16	29.8	14.63	12.58
Longleaf pine	1.21	8.66	23.27	43.48	11.73	17.14	4.39
Pop ash	2.50	4.31	4.92	26.48	36.50	11.88	20.22
Sweetgum	2.32	5.27	7.41	26.17	37.44	11.87	17.11
Water tupelo	2.27	5.73	6.14	26.77	36.85	12.32	17.92

Table 3. Pearson's Correlation Coefficients (r) between Measured Parameters of Litters before Burn. Significant Correlations (p < 0.05) Are Highlighted in Bold.

	<i>WEOC</i>	<i>TN</i>	<i>C/N</i>	<i>UVA</i>	<i>SUVA</i>	<i>E2/E3</i>	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>Specific THM formation</i>
TN	-0.3											
C/N	0.81	-0.74										
UVA	0.79	-0.45	0.75									
SUVA	0.25	-0.47	0.44	0.78								
E2/E3	0.21	-0.51	0.48	-0.2	-0.44							
I	0.39	-0.77	0.72	0.28	0.13	0.6						
II	0.79	0.2	0.34	0.7	0.24	-0.31	-0.21					
III	-0.55	0.7	-0.7	-0.21	0.17	-0.81	-0.82	-0.02				
IV	-0.21	0.21	-0.37	-0.6	-0.80	0.44	-0.26	-0.12	-0.25			
V	-0.63	0.56	-0.71	-0.38	-0.02	-0.48	-0.91	-0.14	0.83	0.17		
Specific THM formation	0.80	-0.35	0.59	0.81	0.41	-0.03	0.1	0.80	-0.38	-0.03	-0.3	
Specific HAN formation	-0.35	0.18	-0.42	-0.67	-0.76	0.45	-0.3	-0.27	-0.16	0.98	0.31	-0.14

Table 4. Pearson's Correlation Coefficients (r) between Measured Parameters of Litters after Burn. Significant Correlations (p < 0.05) Are Highlighted in Bold.

	<i>WEOC</i>	<i>TN</i>	<i>C/N</i>	<i>UVA</i>	<i>SUVA</i>	<i>E2/E3</i>	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>Specific THM formation</i>
TN	0.41											
C/N	0.67	-0.39										
UVA	0.91	0.75	0.31									
SUVA	-0.89	-0.01	-0.87	-0.63								
E2/E3	0.81	-0.12	0.90	0.53	-0.97							
I	0.88	0.03	0.85	0.64	-0.99	0.93						
II	0.92	0.08	0.84	0.68	-0.98	0.92	0.98					
III	-0.89	-0.04	-0.84	-0.64	0.98	-0.91	-0.99	-1.00				
IV	0.92	0.28	0.68	0.77	-0.94	0.84	0.96	0.96	-0.96			
V	-0.93	-0.17	-0.79	-0.74	0.98	-0.92	-0.99	-0.97	0.97	-0.97		
Specific THM formation	-0.27	0.15	-0.36	-0.09	0.23	-0.15	-0.24	-0.36	0.36	-0.23	0.16	
Specific HAN formation	-0.73	-0.48	-0.32	-0.72	0.72	-0.67	-0.71	-0.69	0.68	-0.82	0.78	-0.28

In other words, raw litter extracts have much less humic acid and fulvic acid-like compounds in comparison to black carbon extracts. Longleaf pine had the lowest increase both in region III and V after burn and also the lowest decrease in region I. It also had the lowest weight loss and DOC decrease, suggesting that longleaf shows significantly fewer changes both in carbon quality and quantity after burn in comparison to other studied species. It is in accordance with its classification as a “fire-resistant” species. Resistance against fire is mainly due to its moist and dense needles (54).

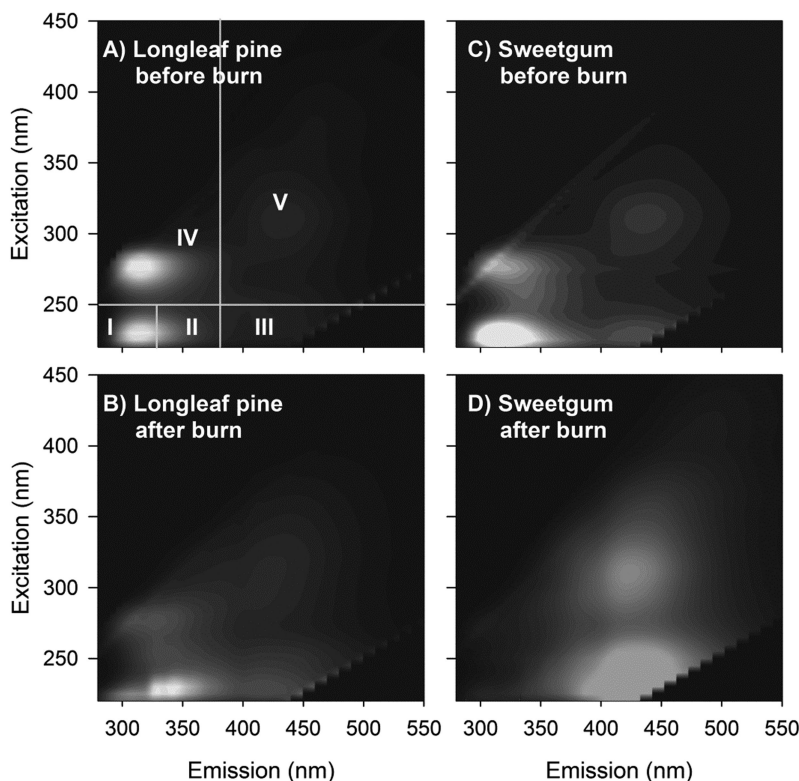


Figure 2. Fluorescence emission-excitation matrix of longleaf pine and sweetgum water extracts before and after burn.

Effect of Prescribed Burning on Formation of Disinfection By-Products

DOC has been implicated as a primary contributor to the formation of THMs (19), while dissolved organic nitrogen has been identified as a precursor to both THMs and N-DBPs (e.g., HANs) during drinking water purification (55). However, little is known about how BC (burned litters) contributes to DBP formation. As shown in our results, chloroform was the major DBP species after

chlorination for all plant species (Figure 3). For the original litters before burn, the specific chloroform formation followed the order: sweetgum (8.34 ± 1.11 mmol/mol-C) > baldcypress (4.67 ± 0.18 mmol/mol-C) = water tupelo (4.45 ± 0.21 mmol/mol-C) > longleaf pine (3.61 ± 0.17 mmol/mol-C) > boxelder (2.99 ± 0.06 mmol/mol-C) > pop ash (2.59 ± 0.03 mmol/mol-C). The dichlorobromomethane was the other detectable THM species, with similar specific formation (0.008-0.011 mmol/mol-C) among all original unburned litters. For the HAN, dichloroacetonitrile and trichloroacetonitrile were the only two detectable species. The specific dichloroacetonitrile formation followed: boxelder (0.214 ± 0.003 mmol/mol-C) > pop ash (0.137 ± 0.001 mmol/mol-C) > baldcypress (0.127 ± 0.008 mmol/mol-C) > longleaf pine (0.092 ± 0.011 mmol/mol-C) > sweetgum (0.083 ± 0.006 mmol/mol-C) > water tupelo (0.066 ± 0.004 mmol/mol-C). The specific trichloroacetonitrile formation was much lower than dichloroacetonitrile, which was highest for boxelder (0.007 ± 0.000 mmol/mol-C) and did not show difference among other plant species (0.003-0.005 mmol/mol-C).

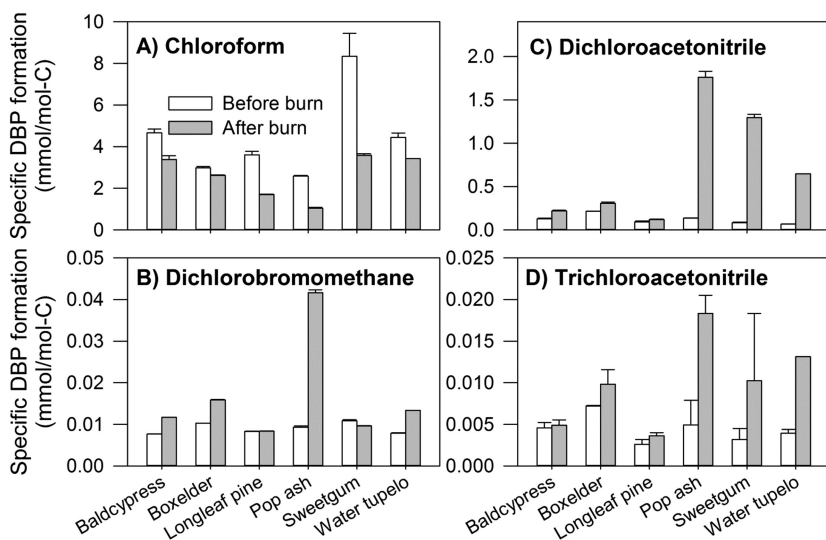


Figure 3. Chlorine reactivity of dissolved organic carbon extracted from litter materials as indicated by the specific DBP formation.

After burning, both the specific THM formation and specific HAN formation were significantly altered, which is in agreement with the results of field studies of prescribed fire (Part II) and wildfire. The specific chloroform formation decreased by 12%-60% for all plant species (56). However, the specific dichlorobromomethane formation increased for baldcypress (52%), boxelder (55%), pop ash (347%), and water tupelo (69%). Different from chloroform, the specific haloacetonitriles formation increased for all species. While the specific dichloroacetonitrile formation increased by 30%-1457%, the specific trichloroacetonitrile formation increased by 7%-73%. There was no correlation between the percent decrease of specific THM formation and the percent decrease

of specific HAN formation, suggesting that the fire's effects on the THM precursor and HAN precursor were independent. However, correlation between specific HAN formation and percent fluorescence response of region IV was significant for both before and after burn (Table 3). This may provide a fast easy method for prediction of specific HAN formation both before and after burn.

Multiplying the specific DBP formation with the WEOC, we can estimate the DBP precursor yield ($\mu\text{g/g}$ -original-litter) from the litter material (Figure 4). Before burn, the litter materials can potentially produce THMs ranging from 82.3 ± 1.0 $\mu\text{g-THMs/g}$ -original-litter (pop ash) to 706.4 ± 93.7 $\mu\text{g-THMs/g}$ -original-litter (sweetgum). After burn, the THM yield decreased by 70%-98% for all species (Figure 4a). For HANs, these litter materials had the HAN yield ranging from 3.72 ± 0.24 $\mu\text{g-HANs/g}$ -original-litter (water tupelo) to 10.40 ± 0.14 $\mu\text{g-HANs/g}$ -original-litter (boxelder). As the specific HAN formation has increased after burn, there was a much less decrease in HAN yield compared to THM yield after burn. The HAN yield dropped by 29%-69%, for all species (Figure 4b).

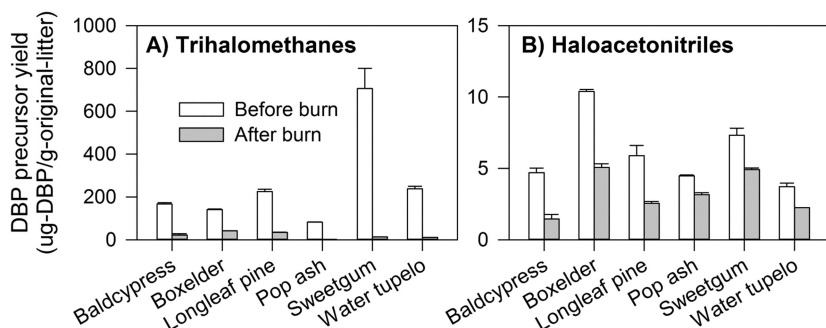


Figure 4. The disinfection by-product yields as in trihalomethane (A) and haloacetonitriles (B) before and after burn at 340 °C. The yield calculations were based on the original unburned biomass.

The results demonstrated the effects of low intensity burning (i.e. 340 °C) on changes in quantity and quality of DBP precursors on the forest floor. Because fire can largely consume organic matter in detritus layer, WEOM (i.e. WEOC and WETN) decreased after burn. Such consumption of litter materials is likely an overriding effect to reduce the DBP precursors, which resulted in the overall reduction in DBP yield from litter materials (Figure 4). Chlorine reactivity of the burned litter in forming HANs is much higher than that of original litter. As the HANs have been documented to be much more toxic than the common carbonaceous DBPs such as THMs and haloacetic acids, attention should be placed on the nitrogenous DBPs in water treatment of fire-affected DOM.

The study revealed the effect of vegetation cover on the potential DBP export. We found that among the major plant species within the watershed, the sweetgum has a much larger content of DBP precursor because its litter has high WEOM that is also very reactive in forming DBPs (ranking 1st for THM

yield and the 2nd for HAN yield; Figure 4). In contrast, the pop ash is a species with much less contribution to the watershed export of DBP precursor, with only 12% THM formation and 61% HAN formation relative to the sweetgum. The response of DBP precursors in litter materials is highly dependent upon plant species as shown in Figure 4. Therefore, the knowledge acquired in one watershed about the fire effect on the DBP export may not be directly applicable to estimate the DBP export in another watershed that has quite different dominant plant species. The controlled lab study here is designed for elucidating the effects of simulated burning on the DBP precursor in litter materials without any interference from other environmental factors such as mixes of vegetations, fuel moistures, decomposition stages, etc. To evaluate a real situation on DBP precursor production from a burnt forest, our research team conducted a controlled burning experiment and natural exposure of WEOM in a natural forest at Hobcaw Bonary, Georgetown SC. Results and findings of the controlled field study, as the Part II of this prescribed fire study, are discussed in the following chapter.

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Appendix

Table A1. The Categorization of Pyrogenic Products from Results of Pyrolysis Gas Chromatography Mass Spectrometry: Ar = aromatics; Lg = lignins; Lp = lipids; Ps = polysaccharides; N = nitrogens; PAHs = polycyclic aromatic hydrocarbons; Ph = phenolics.

#	Compound	Type	#	Compound	Type
1	Phenol, 2-methoxy-	Lg	77	Heptadecane	Lp
2	Phenol, 2-methoxy-4-methyl-	Lg	78	1-Eicosene	Lp
3	Phenol, 4-methoxy-3-methyl-	Lg	79	1-Nonene	Lp
4	1,2-Benzenediol, 3-methoxy-	Lg	80	Tridecane	Lp
5	Phenol, 4-ethyl-2-methoxy-	Lg	81	Heptadecane	Lp
6	4-Hydroxy-3-methoxystyrene	Lg	82	Toluene	Ar
7	Phenol, 3-methoxy-5-methyl-	Lg	83	Ethylbenzene	Ar
8	Phenol, 2,6-dimethoxy-	Lg	84	P-Xylene	Ar
9	Phenol, 2-methoxy-4-(1-propenyl)-	Lg	85	P-Xylene	Ar

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Table A1. (Continued). The Categorization of Pyrogenic Products from Results of Pyrolysis Gas Chromatography Mass Spectrometry: Ar = aromatics; Lg = lignins; Lp = lipids; Ps = polysaccharides; N = nitrogens; PAHs = polycyclic aromatic hydrocarbons; Ph = phenolics.

#	Compound	Type	#	Compound	Type
10	3,4-Dimethoxyphenol	Lg	86	Benzene, Propyl-	Ar
11	Vanillin	Lg	87	4-Ethyltoluene	Ar
12	Eugenol	Lg	88	1,2,4-Trimethylbenzene	Ar
13	Phenol,2-methoxy-4-(1E)-1-propenyl-	Lg	89	2-Ethyltoluene	Ar
14	4-methoxy-3-hydroxyacetophenone	Lg	90	2-Methylstyrene	Ar
15	3-methoxy-2,4,6-trimethylphenol	Lg	91	Benzene,1-methyl-2-(1-methylethyl)-	Ar
16	2-Propanone,1-(4-hydroxy-3-methoxyphenyl)-	Lg	92	Benzene, 2-propenyl	Ar
17	Phenol,2,6-dimethoxy-4-(2-propenyl)-	Lg	93	Benzene,1-methyl-4-(1-methylethenyl)-	Ar
18	3,5-Dimethoxy-4-hydroxybenzaldehyde	Lg	94	Benzene, 1-butenyl-	Ar
19	Phenol,2,6-dimethoxy-4-(2-propenyl)-	Lg	95	Benzene,(1-methylene-2-propenyl)	Ar
20	4-Ethyl-2-methoxyphenol	Lg	96	Resorcinol	Ar
21	1,2,4-Trimethoxybenzene	Lg	97	1-ethyl-2,4,5-trimethylbenzene	Ar
22	Phenol, 3,5-dimethoxy-	Lg	98	Benzene, 1,3,5-trimethyl-2-(1,2-propadienyl)-	Ar
23	Vanillyl ethyl ether	Lg	99	Benzene, (1-ethynyl-2-methyl-1-propenyl)-	Ar
24	2,5-Dimethylfuran	Ps	100	Mesitylene	Ar
25	2(5H)-Furanone	Ps	101	Benzene	Ar
26	Furfural	Ps	102	Benzene, 1-propynyl-	Ar
27	Cyclopentene,1-(1-methylethyl)-	Ps	103	Cinnamaldehyde	Ar
28	2-Cyclopenten-1-one,2-methyl-	Ps	104	Mesitaldehyde	Ar
29	Furfuryl alcohol	Ps	105	1-Indanone	Ar
30	2-Furancarboxaldehyde,5-methyl-	Ps	106	Benzene, octyl-	Ar

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Table A1. (Continued). The Categorization of Pyrogenic Products from Results of Pyrolysis Gas Chromatography Mass Spectrometry: Ar = aromatics; Lg = lignins; Lp = lipids; Ps = polysaccharides; N = nitrogens; PAHs = polycyclic aromatic hydrocarbons; Ph = phenolics.

#	Compound	Type	#	Compound	Type
31	2(5H)-Furanone,3-methyl-	Ps	107	Phenol	Ph
32	Furan, 2,4-dimethyl-	Ps	108	2,5-Dimethylphenol	Ph
33	2(3H)-Furanone,5-methyl-	Ps	109	Phenol,3,5-dimethyl-	Ph
34	2,5-Dimethyl furane	Ps	110	Phenol,2-ethyl-5-methyl-	Ph
35	Furan, 2-ethenyl-	Ps	111	Phenol,4-ethyl-3-methyl-	Ph
36	2H-Pyran-2-one, 4-ethenyltetrahydro-	Ps	112	Hydroquinone	Ph
37	2H-Pyran-2-one	Ps	113	1,2-Benzenediol,4-methyl-	Ph
38	2-Cyclopenten-1-one,2-methyl-	Ps	114	1,2-Benzenediol,4-ethyl-	Ph
39	2-Acetylfuran	Ps	115	Phenol,4-(2-propen-1-yl)-	Ph
40	2(3H)-Furanone	Ps	116	1,4-Benzene-diol,dimethyl-	Ph
41	2H-Pyran-2-one, 5,6-dihydro-3,5,5-trimethyl-	Ps	117	1,2-Benzenediol,4-ethyl-	Ph
42	Furfuryl alcohol	Ps	118	Pyrogallol	Ph
43	3-Methyl-2-cyclopenten-1-one	Ps	119	Methylparaben	Ph
44	2-Cyclopenten-1-one,2,3-dimethyl-	Ps	120	1,4-Benzenediol,2,3,5,6-tetramethyl-	Ph
45	2-Cyclopentenone	Ps	121	1,2-Benzenediol,4-methyl-	Ph
46	Pyridine	N	122	1,3-Benzenediol,4-ethyl-	Ph
47	Benzonitrile	N	123	Pyrogallol	Ph
48	Oxazole,2-ethyl-4,5-dihydro-	N	124	1,4-Benzenediol,2,3,5-trimethyl-	Ph
49	1H-Pyrrole, 1-methyl-	N	125	m-Tolualdehyde	Ph
50	N-Methyl pyrrole	N	126	3-Ethylphenol	Ph
51	Pyrrole	N	127	Phenol,2-methyl-	Ph
52	2-Oxocyclohexanepropiononitrile	N	128	Phenol,4-methyl-	Ph
54	3-Pyrazolidinone, 1,4-dimethyl-	N	129	2,3-Dimethylphenol	Ph

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Table A1. (Continued). The Categorization of Pyrogenic Products from Results of Pyrolysis Gas Chromatography Mass Spectrometry: Ar = aromatics; Lg = lignins; Lp = lipids; Ps = polysaccharides; N = nitrogens; PAHs = polycyclic aromatic hydrocarbons; Ph = phenolics.

#	Compound	Type	#	Compound	Type
55	Perillartine	N	130	2,3-Dimethylphenol	Ph
56	3-Methylpyrazole	N	131	3,5-Dimethylphenol	Ph
57	Benzyl cyanide	N	132	2,5-Dimethylphenol	Ph
58	3-Methylindole	N	133	3-Ethylphenol	Ph
59	Benzeneethanamine,4-ethyl-2,5-dimethoxy-a-methyl-	N	134	Pyrocatechol	Ph
60	Pyridine, 3-methyl-	N	135	1,2-Benzenediol,3-methyl-	Ph
61	3-Methylpyrrole	N	136	4-Methylcatechol	Ph
62	Pyrazine, 2,3 dimethyl-5-(1-Propenyl)-	N	137	4-Ethylresorcinol	Ph
63	Benzeneethanamine, 2,5-dimethoxy-	N	138	1,4-Benzenediol,2,3,5-trimethyl-	Ph
64	Pyrazine, tetraethyl-	N	139	Naphthalene	PAHs
65	6-Hydroxy-1,2,3,4-tetrahydroisoquinoline-1-carboxylic acid	N	140	2-Methylnaphthalene	PAHs
66	1H-Indole, 4-(3-methyl-2-butenyl)-	N	141	2-Methylnaphthalene	PAHs
67	Undecane	Lp	142	Naphthalene,1,2-dimethyl-	PAHs
68	Tetradecane	Lp	143	2,6-Dimethylnaphthalene	PAHs
69	Nonadecane	Lp	144	Naphthalene,1,6,7-trimethyl-	PAHs
70	1-Hexacosene	Lp	145	Naphthalene,1,6,7-trimethyl-	PAHs
71	Heptadecane	Lp	146	1-Methylnaphthalene	PAHs
72	1-Eicosene	Lp	147	Biphenyl	PAHs
73	1-Hexacosene	Lp	148	Naphthalene, 1-ethyl-	PAHs
74	3-Eicosyne	Lp	149	2-Naphthol	PAHs
75	1-Docosene	Lp	150	Dibenzofuran	PAHs
76	1-Nonadecene	Lp	151	Carbaryl	PAHs
			152	Fluorene	PAHs

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